

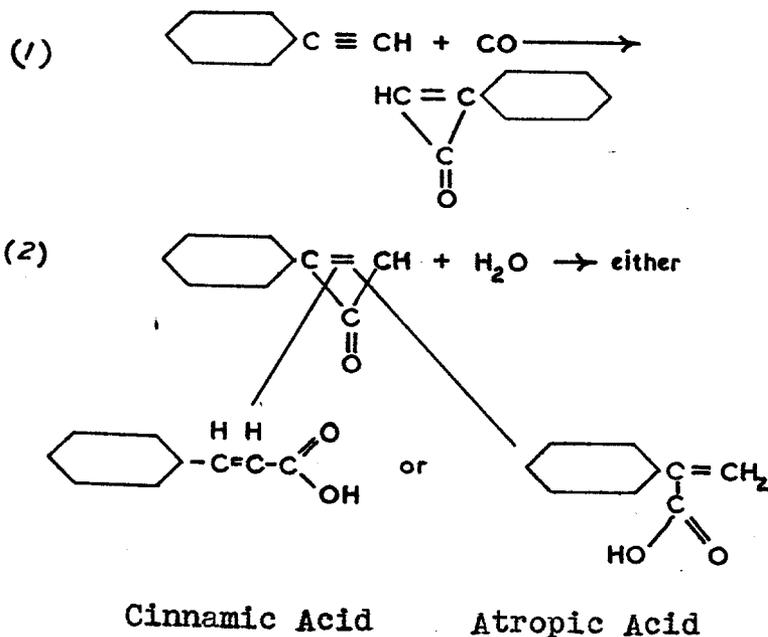
Propargyl alcohol can be partially hydrogenated to give allyl alcohol and further n-propyl alcohol in neutral or alkaline solution; in acid solution by hydrogenation the propargyl alcohol converts to propionaldehyde. Allyl alcohol can be converted to glycerine either by treatment with hydrogen peroxide (or persalts) or by the conventional method with chlorine and water. For the hydrogenation step Fe can serve as the catalyst and for the H_2O_2 oxidation to glycerine selenic acid is employed.

Carbonylation.

Carbonylation is the name given to reactions wherein carbon monoxide is added to another compound, for example to acetylene, olefine, cyclic oxide, and the like, along with such a hydrogen-containing compound as H_2 , H_2O , ROH, NH_3 , RSH, etc. These reactions include the OXO reaction (olefines + CO + H_2) as a special case. In this reaction, olefines in liquid phase are reacted with CO + H_2 in the presence of the Fischer-Tropsch cobalt catalyst to give a mixture of aldehydes, having more carbon atoms than the employed olefines; the aldehydes are thereafter hydrogenated to alcohols for separation by distillation. A characteristic of this process resides in the fact that, due to the shift of olefinic double bond along the hydrocarbon chain during the reaction (isomerization), a multiplicity of isomers of the produced branched and normal alcohols is formed. Separation of a single compound in pure form is difficult if not impossible even when a single olefine is that starting material. This result seems to be a property of the cobalt catalyst.

Dr. Reppe prefers to use as the catalysts Nickel Carbonyl ($Ni(CO)_4$) or Iron Carbonyl ($Fe(CO)_5$) and H_2O instead of H_2 when the desired end-product is alcohols; by means of this advance, Reppe produces from a given olefine, or the like, a mixture of two isomeric carboxy acids having each one more carbon atom than the employed starting material, the acids can then be reduced to corresponding alcohols or aldehydes if they are the desired products. The said acid isomers are usually straight chain and alpha substituted acids if the employed olefine is a straight-chained compound.

unsaturated bond of the hydrocarbon to form the propenone ring because there thus exists the possibility of severing the ring at either carbon valence of its CO-group; for example, when reacting phenyl acetylene with CO - H₂O, the reaction may progress as follows:



Oleic olefine reacts as above to give corresponding fatty acids.

As aforementioned, these carbonylations can be carried out with Ni(CO)₄ added to the reactor or it may be formed in situ from such soluble nickel salt as nickel chloride activated with sodium iodide - said carbonyl being formed under the pressure conditions of reaction.

In the preparation of propionic acid from C₂H₄, CO and H₂O, said acid is formed as follows: into a reactor maintained at about 235°C-280°C. and at a pressure of 250-300 atm., CO, C₂H₄ and H₂O are introduced at the bottom thereof, said reactor also containing elemental nickel or nickel acetate. Ni(CO)₄ is formed from said nickel or its compound by reactions with the inflowing CO. In the case of ethylene, as the unsaturated hydrocarbon, no solvent or liquid phase is necessarily present in the

665

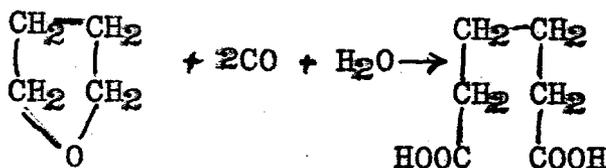
reactor although it is of advantage. The reactor can be made with a lining of absolutely pure copper; iodine or other halogens are not necessary but they have an advantage if apparatus resistant to them are developed - which copper is not. The use of the halogens has the disadvantage that they must be eliminated from the product.

The propionic acid formed in the reactor upon removal therefore contains some $\text{Ni}(\text{CO})_4$ which can be removed therefrom by volatilization - it is very poisonous and boils at 45°C . and decomposes in the air. Fractional condensation has been found effective in performing the separation - the separated $\text{Ni}(\text{CO})_4$ can be returned to the process.

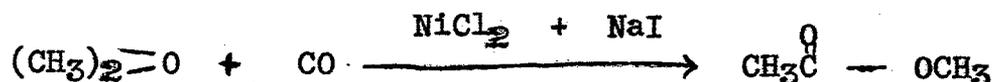
When the employed unsaturated hydrocarbon is propylene or butylene, it is necessary to employ a solvent, such as the formed acid in the reactor; in the case of the higher olefines (such as produce fatty acids) the use of a solvent is not necessary probably because of their high boiling points.

From ethylene up to 95% yield of propionic acid is obtained.

Not only can monocarboxylic acids be made from olefines but also from alcohols, and polycarboxylic acids are preparable from CO and the glycols as well as from cyclic ethers of the latter. For example, Hexandiol 1,6 smoothly reacts to Suberic acid; and Tetrahydrofuran with $\text{CO} + \text{H}_2\text{O}$ converts to Adipic acid in the presence of the above metal carbonyls as follows:-



Although not specifically so-stated by Dr. Reppe, it may be assumed, from his above statement, that methyl acetate can be formed from methyl ether -

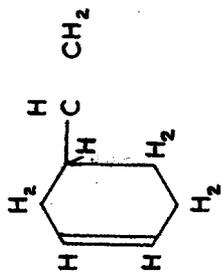
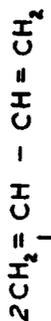


The above carbonylation of the THF is carried out in continuous operation in the liquid phase with NiCl_2 and NaI as catalyst at 200 atm. and 270°C . In an 8-liter reactor, 40 liters/hour of CO , measured at 200 atm., is passed counter-current to a downward flow of 300-600 cc/hour of a 10% aqueous solution of THF containing 1% of NaI , the CO being recycled; the conversion of THF to adipic acid is better than 90%.

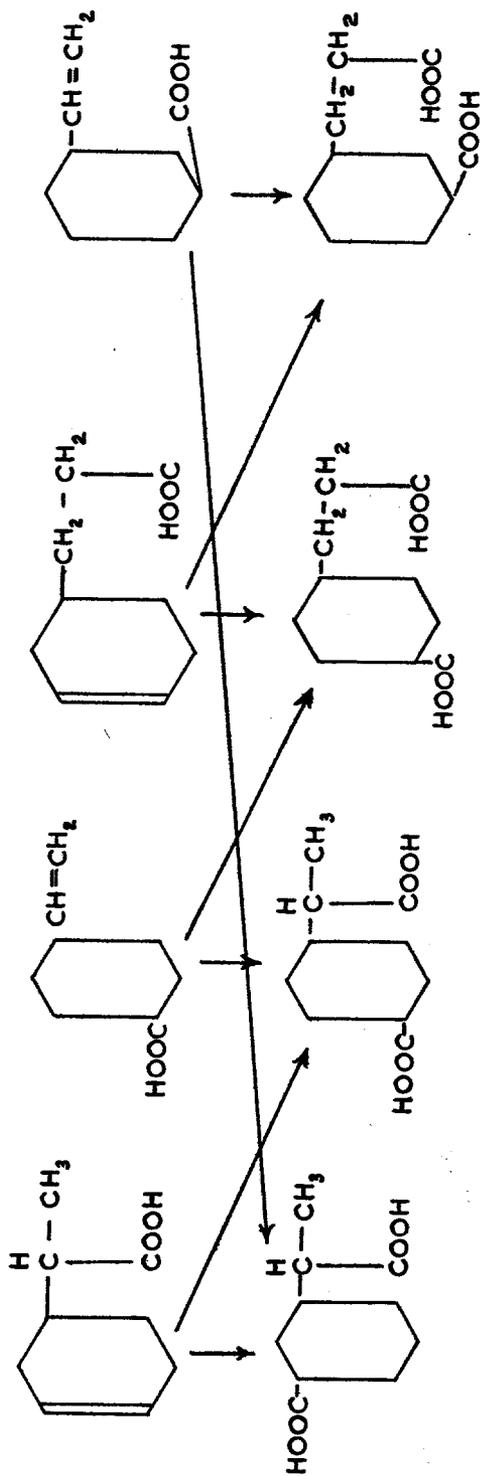
The diolefin, butadiene, reacts with CO and H_2O in the presence of $\text{Ni}(\text{CO})_4$, giving a 70%-90% yield of fatty acids at 200 atm. pressure and about 270°C . The reaction is good for the manufacture of poly-amides to make high polymers of the Nylon-type. The reaction proceeds along rather complicated courses giving a multiplicity of closely-related products. Firstly, under the conditions of reaction, butadiene condenses with itself to form vinyl cyclohexene which then carbonylates at the unsaturated bonds to give carboxy-acids, as shown on the next page.

665

VINYL CYCLOHEXENE



$\text{CO} + \text{H}_2\text{O}$



665

The commercial development of these carbonylations was held up for lack of acid-resisting materials of construction that were not available in Germany during the war.

Synthesis of Alcohols from Water and Olefines.

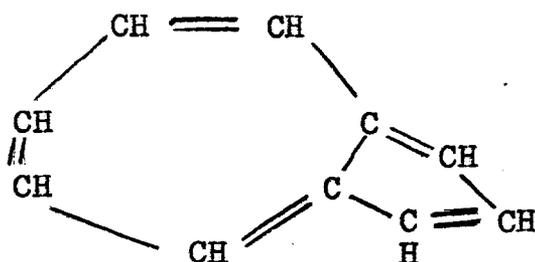
At a pressure from 200-300 atm. and a temperature of 300°C. for ethylene and about 250°C. for propylene, these unsaturateds can be converted directly to alcohols by reaction with water in the presence of tungsten oxide supported on silica gel. The tungsten oxide forms about 20% of the catalyst by weight. The higher the pressure employed, the better. Tungsten Trioxide (WO_3) is inoperative but must be reduced at 600°C. to W_2O_5 before starting; about 5% ZnO in methylamine solution promotes the catalyst.

In practising the above process, C_2H_4 , for example, and H_2O are introduced at the above pressure into the top of a reactor tower containing the catalyst which is maintained at the above required temperature. From the bottom of the reactor tower, there is withdrawn into an expansion vessel, about a 20% aqueous solution of the formed alcohol. Molybdenum is also operative for the same purpose, but is not as good as the tungsten.

When propylene or butylene are used in the above reactions, the secondary alcohols are produced.

Cyclopolyolefines.

Dr. Reppe discussed his recent developments in the field of cyclopolyolefines, a development that may have only scientific interest, but may have wide future application. He has done extensive research to establish the structural formula of especially C_8H_8 - cyclooctatetraen, which is the counterpart of C_6H_6 in the benzene series of compounds. It is now indisputably established that this compound has the structure -



Azulen has a m.p. of 99.5° in the absolutely pure form in which Dr. Reppe has prepared it.

Physical Properties of the Cyclopolylefines.

<u>Name.</u>	<u>B.P.</u>	<u>Color.</u>
1) Cyclooctatetraene	142-30°C. at 760 mm.	Golden Yellow
2) Cyclodecapentaene	190-195°C. " " at 2 mm. 48-50°C.	Orange
3) Cyclododecahexaene	230-235°C. at 760 mm. 60-65°C at 0.5 mm.	Bright Yellow

The constitution of the latter two compounds has not been definitely established.

These compounds have no practical value; they have been investigated pharmacologically and no essential action established by their use. However, Prof. Kuhn at Heidelberg in the case of the $C_{12}H_{12}$ fraction (b.p. 230°C. to 235°C. and colored deep-blue with some azulene - about 3%) determined that the increases of certain pathological bacteria were completely suppressed in dilution of said fraction of 1:100,000.

Dr. Reppe said that the $C_{10}H_{10}$ fraction called cyclodecapentaene did not yield an oxidation sebacic acid and he believes that the compound may be instead vinyl cyclooctatetraene.

Samples of the above three fractions and of the refined azulene prepared by Dr. Reppe were obtained by members of CIOS Trip No. 215 - Ministry of Supply.

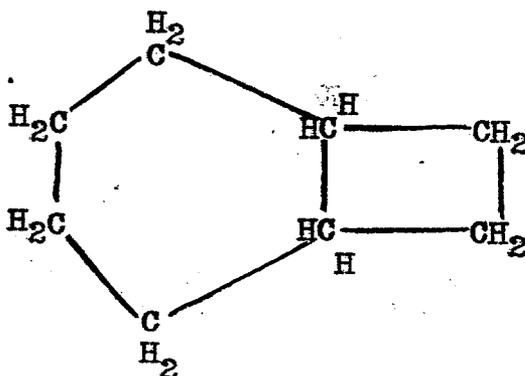
665

In consequence of its olefinic character, cyclo-octatetraene is very reactive in the presence of various reagents. It --

1. Easily oxidizes even in the air.
2. Absorbs Halogens quickly.
3. Polymerizes to a dimer and hard resins even with standing.
4. Forms crystalline addition products with aqueous AgNO_3 and cupric-ammonia, chloride solution.
5. Hydrogenates to cyclooctane.

In certain of its reactions, cyclooctatetraene: -

1. Retains its 8-carbon ring structure.
2. Converts to aromatic series forming derivatives of ethylbenzene and p-xylene; phenylacetaldehyde is formed by water suspension of C_8H_8 with, for example, HgSO_4 ; dehydrogenation of C_8H_8 with Se yields p-xylene.
3. Converts to compounds having both a 6- and a 4-carbon ring; for example, upon halogenation (complete) the highest chlorinated compound is formed in $\text{C}_8\text{H}_8\text{Cl}_6$, m.p. 126°C ., and thus shows there has been an extensive change in structure to a derivative of C_8H_{14} . Dr. Reppe showed C_8H_{14} to be -



Bicyclo - [4.2.2] - octane m.p. - 136°C .